

# **SOLUTION CASTING AND MECHANICAL TESTING OF ARABINAN-CELLULOSE NANOCOMPOSITES**

A Senior Project

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California Polytechnic State University, San Luis Obispo

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of the Requirements for the Degree  
Bachelor of Science, Materials Engineering

By

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## Approval Page

Project Title: Solution Casting and Mechanical Testing of Arabinan-Cellulose Nanocomposites

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### CAL POLY STATE UNIVERSITY

#### Materials Engineering Department

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## Abstract

The purpose of this work was to investigate methods to produce consistent, reliable, and testable thin films of arabinan-cellulose nanocomposites. Mechanical properties and composition of the *Opuntia ficus-indica* cactus spines served as motivation for this research. The high specific strength and stiffness, biodegradability, and sustainability of these spines inspired the creation of composites fabricated from the same materials found in cactus spines: arabinan and nanocrystalline cellulose (NCC). Arabinan serves as the matrix material and NCC as the reinforcement. To explore the feasibility of using a non-toxic solvent, different solution casting techniques with water as a solvent were investigated. Ultrasonication was used to disperse the NCC particles within an arabinan-water solution. A straightforward procedure using silicone molds yielded consistent samples that were suitable for tensile testing. SEM imaging showed signs of aggregation NCC particles. Composite stiffness, strength, and strain to break were found to be dependent on drying time, temperature, water content, and weight percent NCC. To obtain samples at similar water content, samples were monitored until any tacky spots on the film surface had completely dried. Composite samples with greater NCC content were found to have a higher strength and modulus compared to pure arabinan. Arabinan reinforced with 5 wt.% NCC had an average tensile strength of 7.66 MPa and stiffness of 309.03 MPa, while pure arabinan had 4.62 MPa and 211.37 MPa, respectively.

# **1. Introduction**

## **1.1 Motivation**

In the US, packaging waste accounts for a high percentage of all waste. Over the last two decades, consumer packaging accounted for over 20% of US landfill waste, and only a small percentage is recycled. Waiting for landfill waste to degrade is not a realistic goal; some plastic waste takes hundreds of years to fully degrade. Additionally, during the degradation process, plastics and other packaging materials can release toxic chemicals which can affect surrounding ecosystems and contaminate groundwater. To mitigate this problem, a sustainable, biodegradable, and food-safe material could replace current food packaging materials.

A promising materials system sourced from nature fits the criteria. Cactus spines exhibit high specific strength and stiffness, and are entirely composed of non-toxic, food-safe, sustainable, and biodegradable materials: arabinan and cellulose. To verify if manmade arabinan-cellulose composites are feasible and mechanically competitive with current plastics, more characterization is necessary.

## **1.2 Project Goals**

This research project was focused on developing a procedure to reliably fabricate tensile-testable arabinan nanocellulose composites (ARNCCs) inspired from cactus spines. With this procedure, mechanical testing data of ARNCCs at different weight compositions should be obtainable. Instead of building composites from cactus spines, a bottom-up approach using extracted, raw materials will be used to construct a manmade composite using water as a solvent.

## **1.3 Realistic Constraints**

Extracting arabinan from raw materials and producing nanocellulose whiskers was beyond the scope of this project, so raw arabinan had to be purchased through credible suppliers. Additionally, commercially available arabinan is expensive at a price of \$250 for 8 grams. Thus, samples were fabricated and tested for bulk properties as thin films to maximize sample count.

## 2. Background

### 2.1 Cactus Spine Inspiration

Cactus spines are examples of naturally occurring fiber reinforced composites, with cellulose fibers running along the spine's axis surrounded by an arabinan matrix. The cactus species of interest, *Opuntia ficus-indica* (OFI), has notably high spine stiffness with an elastic modulus of  $28 \pm 3.66$  GPa and a density of  $1.3 \text{ g/cm}^3$  [1]. For comparison, glass fiber reinforced polymer (GFRP) has an elastic modulus of 26 GPa and density of  $1.8 \text{ g/cm}^3$  [2]. OFI spines are stiffer yet lighter than typical GFRPs and achieve this with a 50/50 arabinan and cellulose fiber composition [2]. When strength density and stiffness density ratios are plotted (Figure 1), OFI spine mechanical properties are on the order of medium carbon steel [3].

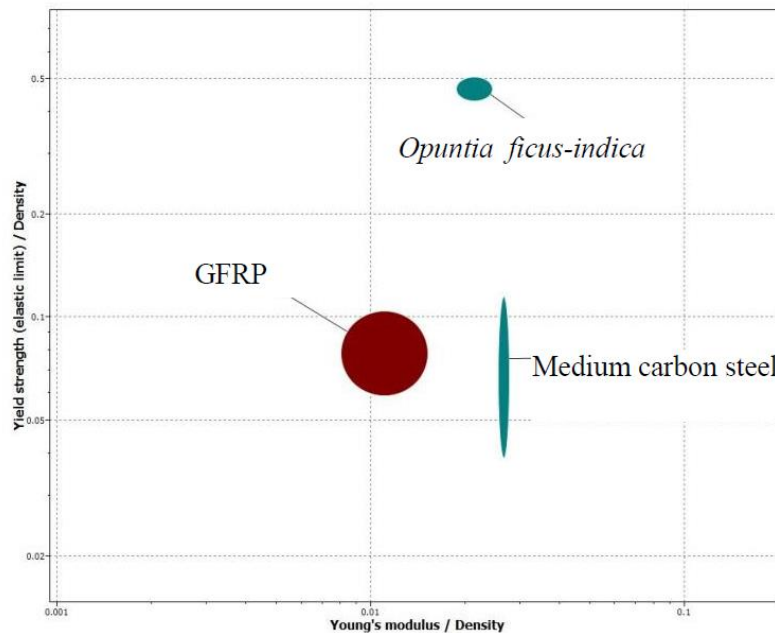


Figure 1 – Graph of specific strength vs. specific modulus for OFI spines, GFRP, and medium carbon steel [3].

OFI spine characterization is accomplished by first fracturing and viewing a spine cross-section under SEM, while XRD is used to determine fiber diameter and crystallinity. Spines analyzed under XRD by Cooper, Goldstein, and Tarlton (2013) suggested that there was no correlation between spine crystallinity and strength. However, the strongest spines tested also had the highest percent crystallinity [4]. This particular investigation only studied 12 species of cacti,

and their testing scale was not large enough to draw conclusions about the relationship between strength, stiffness, and crystallinity. The variance for spine stiffness spanned as large as 20 GPa (Figure 2). This range in stiffness is likely a result of the cellulose content, crystallinity, and fiber orientation.

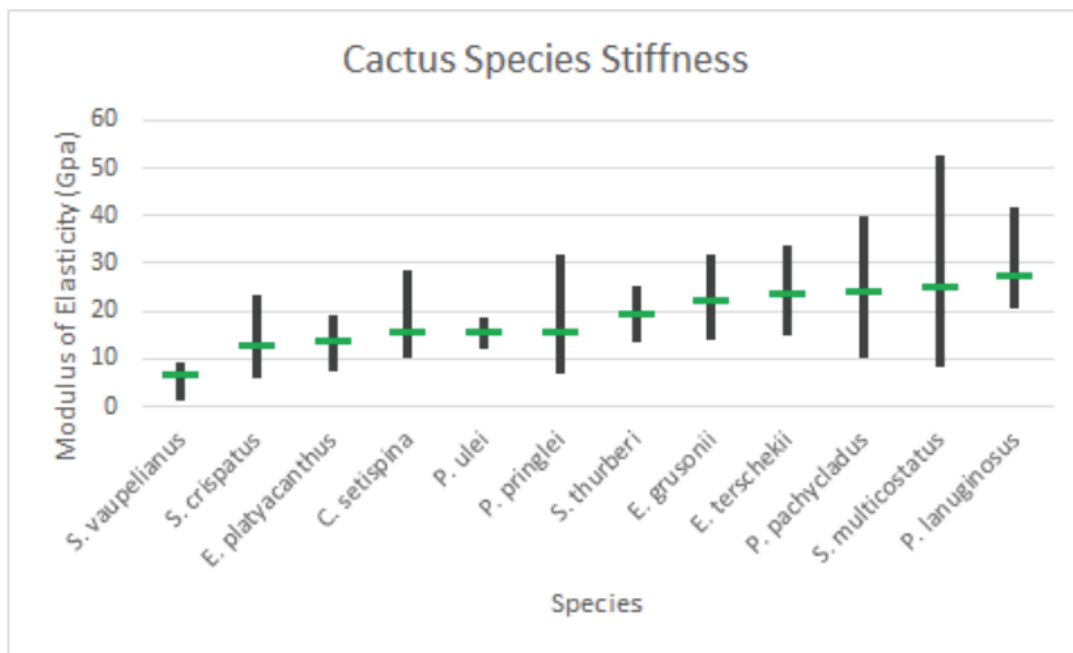


Figure 2 – Mechanical testing data for different species of cacti. Some species have variance twice that of the stiffness. This natural variance makes assumptions about strength-stiffness-crystallinity relationships unclear [4].

## 2.2 Cellulose

Cellulose is a semi-crystalline polysaccharide that is abundantly found in nature. It is a critical structural component in plant cell walls. Its chemical repeat unit is illustrated in Figure 3. The abundance of hydroxyl groups stimulates hydrogen bonding between cellulose chains and arabinan chains. In nature, cellulose is found in cell walls in the form of microfibrils. Microfibrils in turn consist of nanofibrils, or individual chains of cellulose. Figure 4 shows cellulose fibers in a fractured spine. The hydrogen bonding interaction between cellulose and arabinan is the theorized mechanism of how the two compounds interact to form an impressive composite. However, the hydroxyl groups also attract water molecules, which have the potential to damage cellulose fibers by breaking bonds between cellulose repeat units.



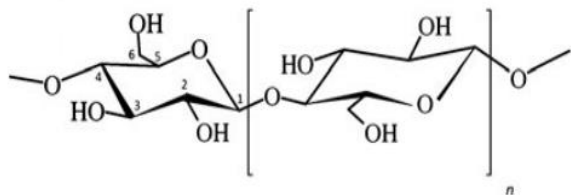
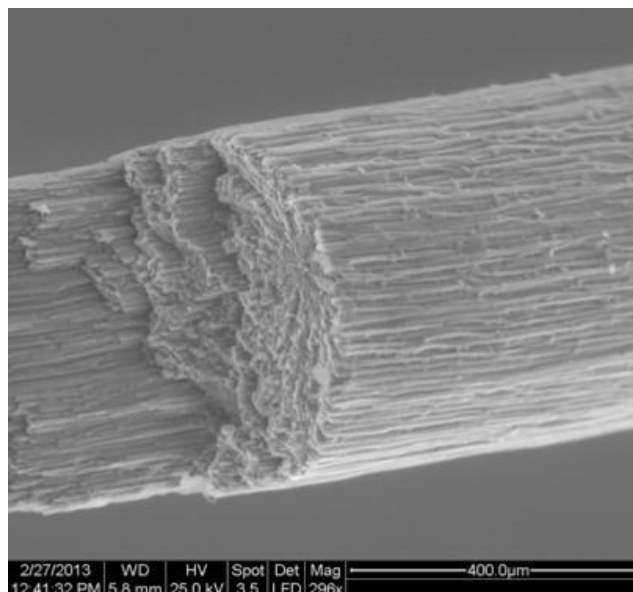


Figure 3 – (Top). A monosaccharide unit of cellulose. Note the abundance of hydroxyl groups that promote hydrogen bonding [5].

Figure 4 – (Right). SEM view of a fractured Mexican Giant Cardon spine (*Pachyereus pringlei*). Cellulose fibers running along the spine are visible [4].



## 2.2.1 Nanocrystalline Cellulose (NCC)

When found in nature, cellulose is a semicrystalline polymer with both crystalline and amorphous regions. To maximize the stiffness of an arabinan and cellulose composite, cellulose reinforcement should be crystalline. To achieve a high crystallinity in cellulose, acid hydrolysis is used to selectively attack amorphous regions of cellulose with sulfuric acid, which occurs spontaneously. The resulting cellulose particles range from 10 to 100s of nanometers in length and 1 to 100 nanometers in diameter [3]. The remaining crystalline regions are known as cellulose nanowhiskers (Figure 5).

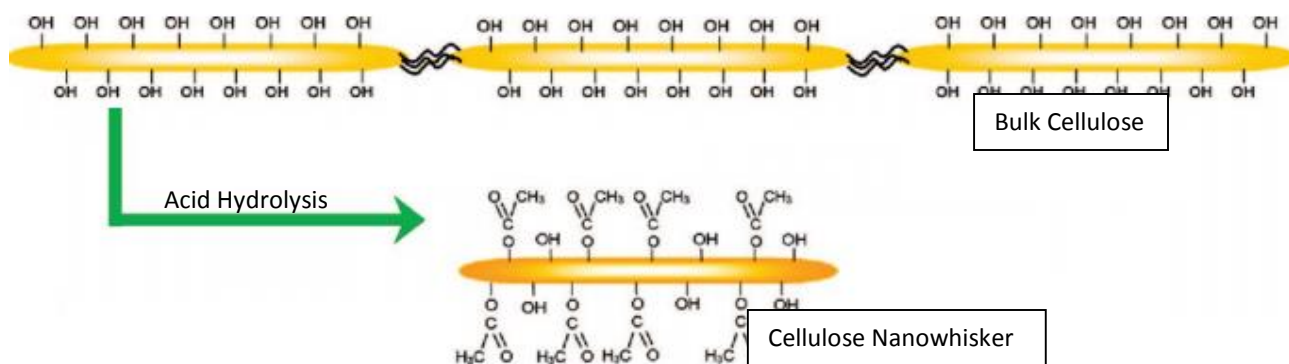


Figure 5 – Schematic of how individual crystalline regions of cellulose are isolated by acid hydrolysis using sulfuric acid to attack the amorphous regions of cellulose, leaving behind the crystalline whiskers that will eventually be used as a composite fiber [6].

The estimated elastic modulus along the whisker axis is as high as 167.5 GPa [7]. In addition, the theorized specific modulus of cellulose is  $67 \text{ GPa cm}^3 \text{ g}^{-1}$ , which is among the highest of all natural materials [5]. However, a notable difference between cactus spines and arabinan nanocellulose composites is that the resulting material is isotropic, since nano-sized cellulose particles are used and microfibrils are not present. To ensure that the nanocrystalline cellulose used in our composites is consistent and verified to specifications, commercially available nanocrystalline cellulose was obtained from Celluforce Inc. This way, a potential source of error is eliminated, time is saved, and there is no need for hazardous reagents like sulfuric acid to be used.

### 2.2.2 Percolation Theory

Since ARNCCs are not like standard fiber reinforced composites, strengthening mechanisms for ARNCCs are different. Nanocomposites behave according to the percolation theory model, where nanoscale reinforcement particles are dispersed within a matrix [8]. If there are enough dispersed particles, they will form quasi-continuous fibers of NCC that will support the majority of an applied load (Figure 6). The theoretical percolation threshold is around five weight percent cellulose [3].

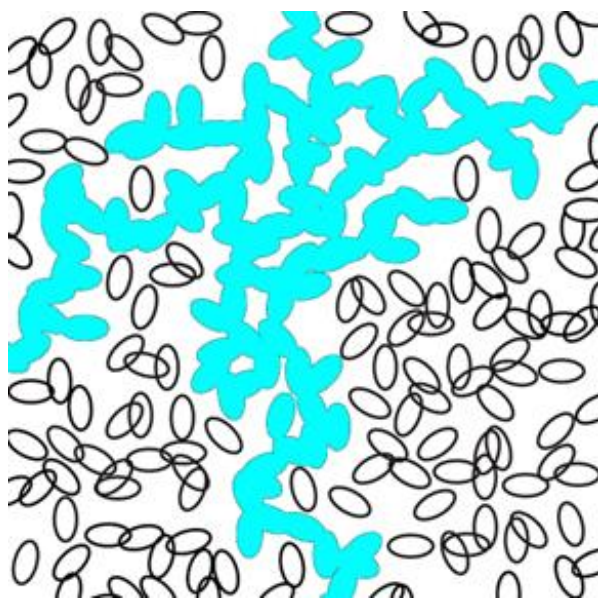


Figure 6 – A diagram depicting a quasi-continuous fiber made from particles shown in blue. These networks help support a load. White particles are not interconnected and thus do not form networks.

## **2.3 Arabinan**

Arabinan, like cellulose, is another biopolymer commonly found in pectin polysaccharide cell walls, and can be found in sugar beets, apples, and of course, cactus spines [3]. Unlike cellulose however, arabinan is a term used to describe a certain complex set of polysaccharides, including arabinose, galactose, and rhamnose. These polysaccharides covalently link together to form a branched biopolymer. Studies of cactus spines suggest that arabinan chains and cellulose chains interact with each other using hydrogen bonding as a primary intermolecular force [9]. Also, this attraction between the arabinan matrix and the cellulose can protect cellulose chains from water damage. Raw arabinan was purchased from Megazyme and was extracted from sugar beets. Megazyme reported that the arabinan composition was 88% arabinose, 3% galactose, 2% rhamnose, and 7% galacturonic acid.

## **2.4 Previous Research**

Previous senior project research teams used dimethylformamide (DMF) to solutionize arabinan and nanocrystalline cellulose in order to solution cast ARNCCs. Dynamic mechanical analysis (DMA) was successful. However, the use of DMF, a toxic solvent, undermines the goal of producing a food-safe, sustainable, and environmentally friendly composite. Thus, the next step was to see the feasibility of using water as a solvent.

Another research team managed to produce samples using water instead of DMF, but they did not add any nanocrystalline cellulose reinforcement to arabinan. Again, DMA testing was used. The DMA instrument at Cal Poly has a limited load cell that can only pull approximately 19N of force, which is not enough to strain ARNCC samples to fracture. Thus, a major goal of this project was to reinforce arabinan with NCC using water as a solvent. Resulting samples should have appropriate geometries so that they can be tensile tested to produce stress-strain curves that showed strain until fracture. Using a developed procedure, this research hopes to shed some light on the relationship between weight percent NCC and strength and stiffness. By testing different weight percent compositions of NCC, the value of the percolation threshold can be identified.

### 3. Experimental

ARNCC composites were fabricated with compositions of 0, 1, 3, and 5 wt. % nanocrystalline cellulose by dissolving NCC and arabinan powder in deionized water at 80°C as indicated in step 1 in Figure 7. Ultrasonic mixing was used to disperse NCC within arabinan. This step is critical, since improper dispersions result in agglomerations of NCC particles that are detrimental to the mechanical properties of the final composite. With ultrasonication, the wetting of individual cellulose whiskers is improved, which is assumed by the percolation strengthening model. Sonicated solutions were stirred for 45 minutes under heat to remove air bubbles that were introduced in the sonication process. Then, solutions were poured into silicone molds that were lined with tape. The addition of tape served to prevent air in the mold from leeching into the drying samples. Samples were dried in an oven at 130°F for 6-9 hours to vaporize water, leaving behind a composite thin film. There was a large spread for drying times, as the ultrasonicator splashes some solution out of the mixing beaker, varying the amount of water in each sample that needed to be dried. This likely did not cause any discrepancies in the data, as drying samples were closely monitored until any tacky spots were completely dry. Thus all samples had similar water content. However, the films were not entirely flat as-cast. It was necessary to trim off flashing to produce a flat, tensile testable sample, as seen in step 7. Using the Mini 55 Instron tensile testing instrument, stress-strain data was acquired.

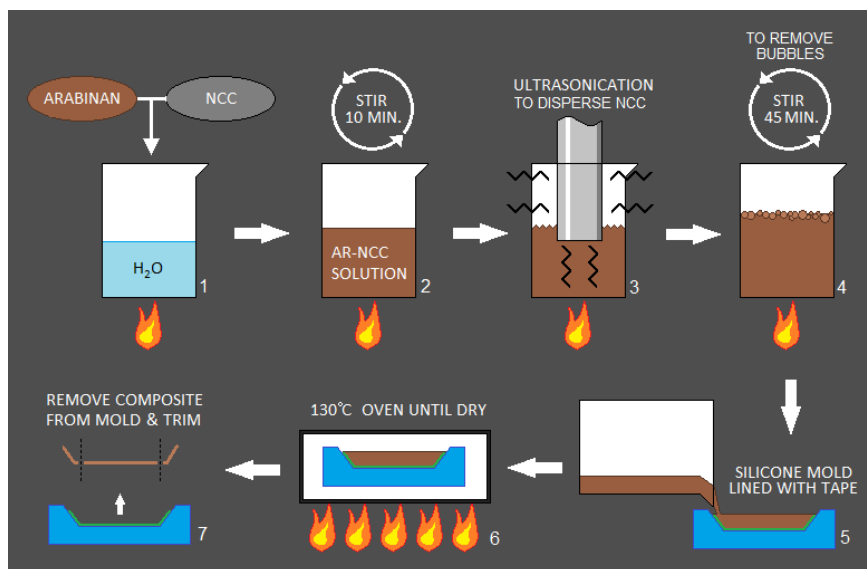


Figure 7 – Diagram outlining the ARNCC solution casting process. See the Appendix for a more detailed procedure.

## 4. Results and Discussion

Strength and stiffness values were obtained through tensile testing. Stress-strain curves can be seen in Figure 8. Right away, it is evident that samples with NCC reinforcement were generally stronger and stiffer than pure arabinan samples. The 1 wt. % NCC samples had the greatest values, averaging at 572.76 MPa for stiffness and 4.62 MPa for strength. More averages are displayed in Table I. However, a strange inconsistency is present in the data. The 3 wt. % NCC had similar mechanical properties to that of pure arabinan. In addition, the 5 wt. % NCC samples had strength and stiffness values between 1 and 3 wt. % NCC samples. So while the addition of NCC was confirmed to reinforce arabinan, percolation theory suggests that strength and stiffness values should increase as more reinforcement is added to the matrix, which does not agree with the data.

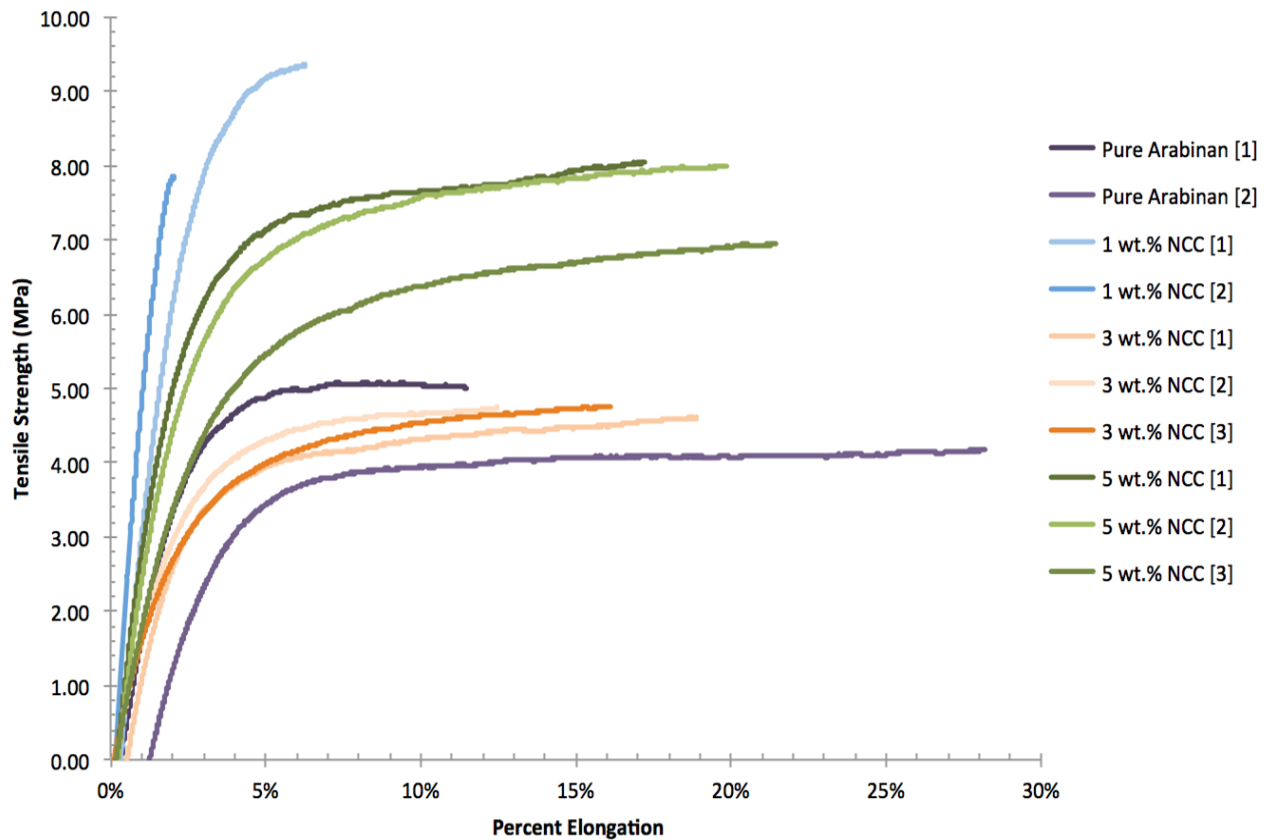


Figure 8 – Stress-strain curves for 0, 1, 3, and 5 wt. % NCC samples.

Table I: Average Modulus and Strength Values for ARNCC Samples

COMPOSITION	AVERAGE MODULUS (MPa)	AVERAGE TENSILE STR(MPa)
Pure Arabinan (0 wt. % NCC)	211.37	4.62
1 wt.% NCC	572.76	8.61
3 wt.% NCC	214.93	4.7
5 wt.% NCC	309.03	7.66

A potential reason why the 3 and 5 wt. % NCC samples had lower mechanical properties than the 1 wt. % NCC samples is that the samples with degraded strength and stiffness values had NCC agglomerations within the matrix. Agglomerations prevent a load-supporting network of NCC from forming, which causes the composite to behave as like pure arabinan, or as if there was no added reinforcement at all. To confirm this, 3 and 5 wt. % NCC fracture surfaces were viewed using scanning electron microscopy (SEM). Particles viewed at 9922x magnification were found (Figure 9).

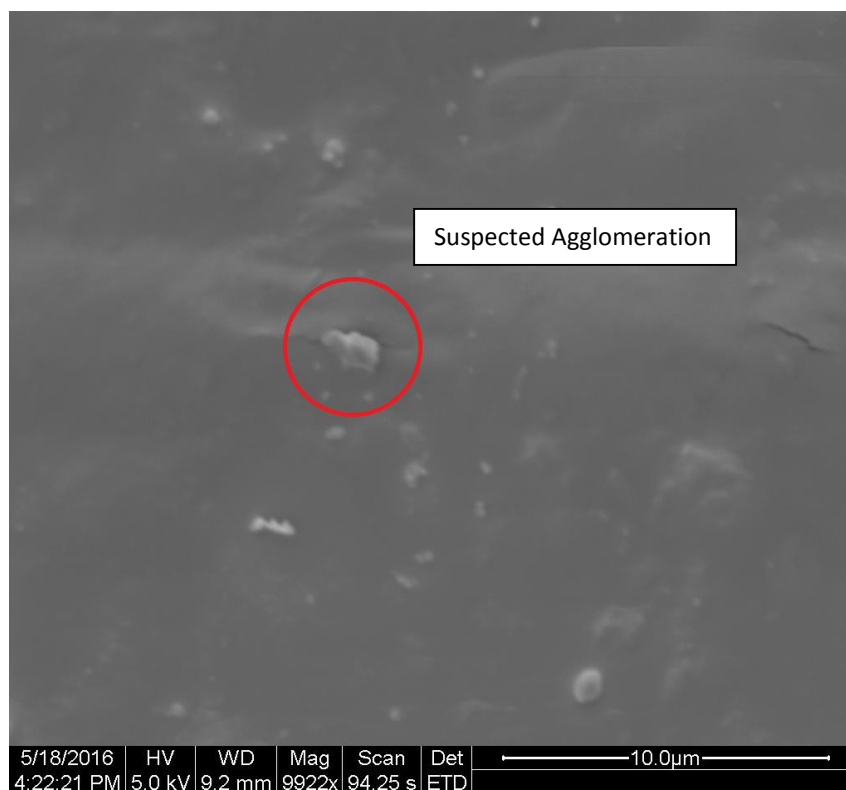


Figure 9 – A suspected agglomeration of NCC particles in the 3 wt. % NCC sample. These agglomerations prevent the composite from having maximum mechanical strength and stiffness. Similar particles were found in the 5 wt. % samples.

Suspicious particles could be seen using SEM, which were assumed to be agglomerations. The existence of these agglomerations explains why the 3 and 5 wt. % NCC samples had worsened mechanical properties than the 1 wt. % NCC samples, even though according to percolation theory, 3 and 5 wt. % should show greater strength than that of 1 wt. %.

If the percolation threshold is assumed to be 1 wt.% NCC, then it is possible to use the percolation model to map composite stiffness vs. reinforcement volume percent. A curve relating the two was generated from the percolation model (Figure 10). The 3 and 5 wt. % NCC samples do not follow the predicted curves for stiffness likely due to the observed agglomerations of NCC viewed under the SEM.

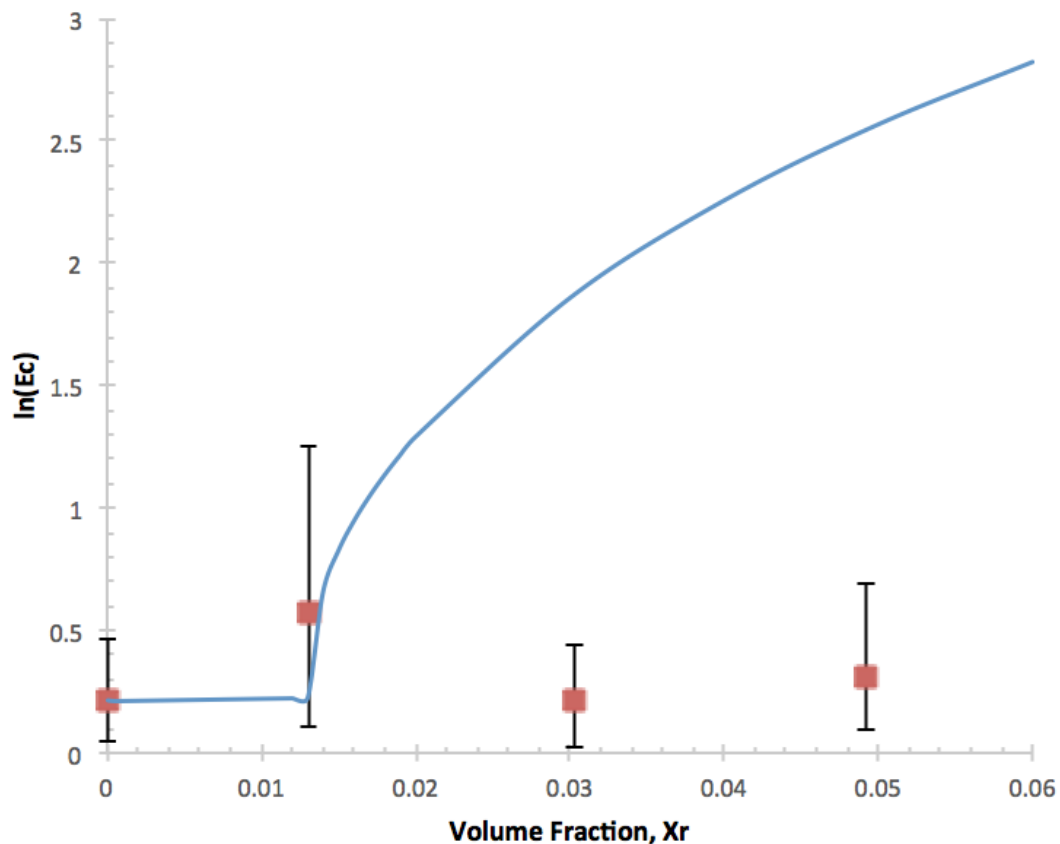


Figure 10 – Shown in blue is the composite elastic modulus related to volume fraction of the reinforcing particles as modeled by the percolation model [8]. The interval plots represent the data spread. This curve assumes the percolation threshold is 1 wt.% NCC. 3 and 5 wt. % NCC do not follow this curve presumably due to agglomeration of NCC particles. Weight percentages were converted to volume fractions using known densities.

## 5. Conclusion

This research project aimed on developing a procedure to reliably fabricate tensile testable ARNCC samples using water as a solvent. There was limited success, as the ultrasonication step was not sufficient to properly disperse the NCC particles within the arabinan matrix. This can be seen in the SEM images. However, using our procedure, the addition of NCC to arabinan did have a reinforcing effect that increased strength and stiffness.

## 6. Recommendations for Future Research Teams

A major issue that limited our research was the cost of arabinan. NCC was not an issue, since very little was used. On the other hand, arabinan was used far more. As of June 2016, the MatE department has zero grams of arabinan remaining, and more must be purchased. It would be extremely helpful if the Chemistry department had a joint project that extracted arabinan from sugar beets and hydrolyzed NCC from bulk cellulose. If this is possible, then ARNCC composites can be made entirely in-house at Cal Poly.

Disregarding the limited supply of arabinan, it would be useful to find the percolation threshold of ARNCCs in water using the procedure we made. To achieve greater precision of weight percent NCC, the total amount of solids can be increased. In addition, more water must be added to the solution if the NCC content exceeds 10 wt. %, as it would be impossible to remove all the bubbles from the thickened solution. In addition, if more water is used, make sure the mold trough has sufficient volume to contain all of the solution. It may be necessary to make a new mold. The current mold has three channels total, so three samples could be casted simultaneously. Silicone was chosen as a mold material, since it was flexible, but consider making a mold from alternate materials like metal. Samples straight out of the oven should be flexible enough to be removed.

Our results also indicated that our dispersion procedure was not sufficient to disperse all of the NCC. Before casting too many samples, make ARNCC samples with longer sonication times. Tensile test, then use SEM to find agglomerates. If there are still agglomerates, then sonicate for longer or find a different dispersion method.



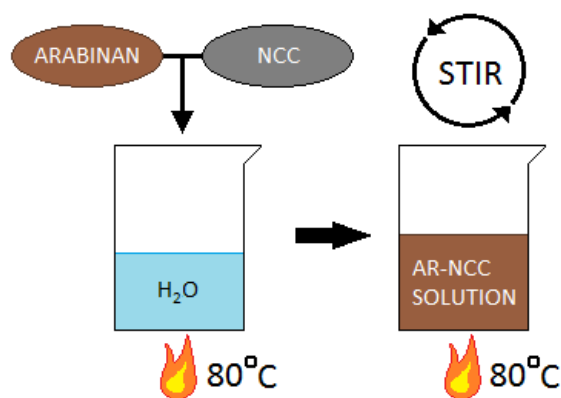
## 7. References

1. Vignon, M.R., Heux, L., Malainine, M.E., and Mahrouz, M. "Arabinan-cellulose composite in *Opuntia ficus-indica* prickly pear spines," *Carbohydrate Research*. 339, 123-331. (2004).
2. Material Properties. *Massachusetts Institute of Technology*. Web. N.d. Retrieved 15 Nov. 2015. <<http://web.mit.edu/course/3/3.11/www/modules/props.pdf>>
3. Johnson, Ross, Rosso, Austin, and Semansky, Nick. "Fabrication and Testing of Arabinan Cellulose Nanocomposites." *Cal Poly Senior Projects* (2014): N. pag. Web, 15 Nov. 2015.
4. Cooper, Mary, Goldstein, and Jeff, Tarlton, Tom. "Strength Testing and Material Characteriation of Cactus Spines." *Cal Poly Senior Projects* (2013): N. pag. Web. 15 Nov. 2013.
5. Huber, Tim, and Owen Curnow. "A Critical Review of All-cellulose Composites." *Journal of Materials Science* 47.3 (2012): 1171-1186. Web. 15 Nov. 2015.
6. Habibi, Yousef, Lucian A. Lucia, and Orlando J. Rojas. "Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications." *Chem. Rev* 110.6 (2010): 3479-3500. Web. 15 Nov. 2015.
7. Bondeson, Daniel, Aji Mathew, And Kristiina Oksman. "Optimization Of the Isolation Of Nanocrystals From Microcrystalline Cellulose by Acid Hydrolysis." *Cellulose* 13 (2006): 171-80. Print.
8. Favier, V, GR Canova, SC Shrivastava, and JY Cavaille. "Mechanical Percolation in Cellulose Whisker Nanocomposites." *Polymer Engineering and Science*, 37.10 (1997): 1732-1739.
9. Malainine, Mohamed E., Alain Dufresne, Daniele Dupeyre, Mostafa Mahrouz, Roger Vuong, and Michel R. Vignon. "Structure and morphology of cladodes and spines of *Opuntia Ficusindica*. Cellulose Extraction and characterization." *Carbohydrate Polymers* 51 (2003):77-83. *Elsevier*. 2003. Web. 3 June 2013.

## 8. Appendix

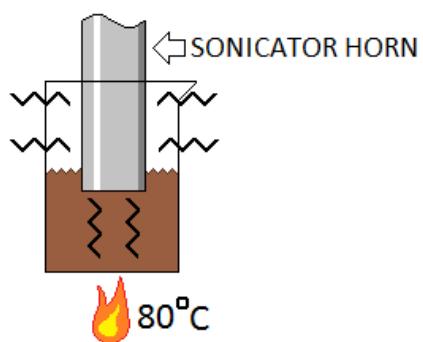
### Arabinan Nanocrystalline Cellulose Composite Fabrication Procedure

**NOTE: READ ALL STEPS BEFORE ATTEMPTING**



#### STEP ONE: Combine Chemicals

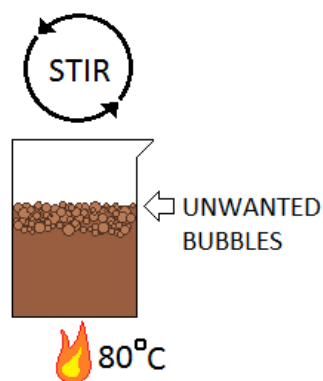
- Homogenize the solution as much as possible before sonication. Total solid mass was 1.5 grams.
- Add 10 mL of DI water for every gram of solid.
  - If no NCC is added, add 6 instead of 10 mL.
  - More water is required for >10 wt. % NCC, otherwise the solution is too thick.
- Stir until no chunks of solid are visible.
- Heat source is a hot plate.



#### STEP TWO: Sonication of Solution

- Disperse NCC in solution
- Pulse 3 sec on, 3 sec off for 5 minutes at 100% amplitude
  - CONSIDER INCREASING SONICATION TIME TO AVOID AGGREGATION OF NCC (Figure 9).
- Warning! Sonication is violent.
  - DO NOT let horn touch the beaker walls. The beaker will shatter.
  - Solution will splash out. Sonicate under a fume food.

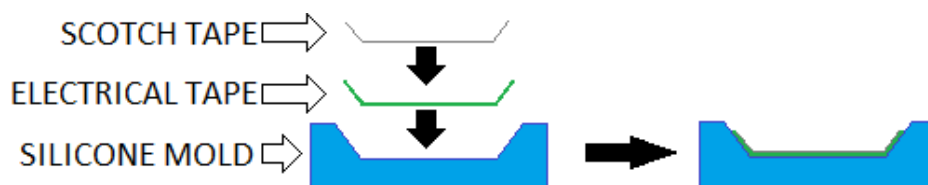
- Heat source is a hot plate.
- SKIP IF NO NCC IS USED



#### STEP THREE: Bubble Removal

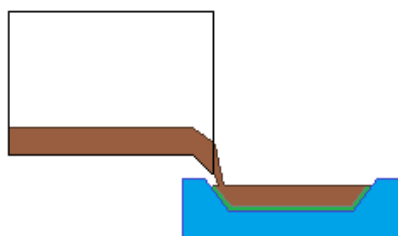
- Sonication will introduce air into the solution.
- Stir under heat for about 45 min, or until all bubbles are gone.
  - Bubbles in the solution may also be present in the final film.
- SKIP IF NO NCC IS USED

#### STEP FOUR: Lining the Mold



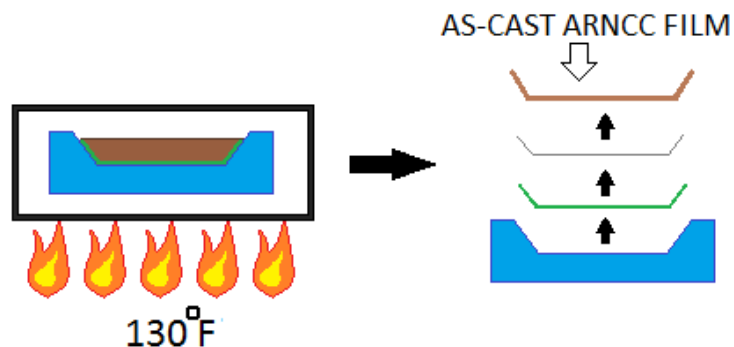
- Line the silicone mold trough with two layers of tape. First, electrical tape, then scotch tape.
  - Electrical tape promotes tape adherence to the mold and scotch tape prevents air from leeching from the mold into the solution
- Make sure there is no air trapped between the mold, the electrical tape, or the scotch tape, as this can cause the final film to not be uniform.

#### STEP FIVE: Solution Casting



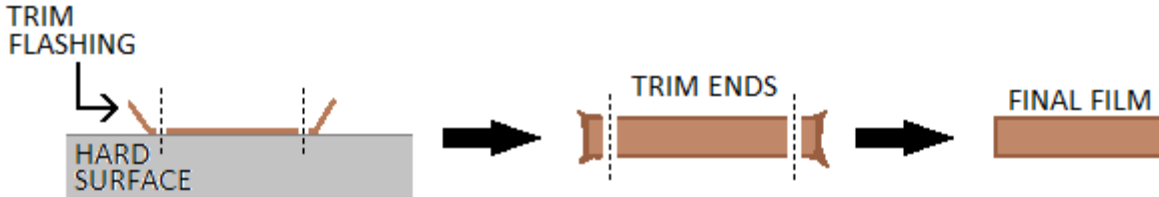
- Pour the solution into the mold that is now lined with tape.
- Try to have the solution spread evenly across the trough. Use a stir rod if necessary.

#### STEP SIX: Drying and Extracting the ARNCC Film



- Oven should be preheated before Step One.
- Make sure the oven rack is balanced so the dried film will have uniform thickness.
- Drying time can be anywhere from 6-9 hours, depending on water content after sonication.
  - To have consistent sample dryness, pull the samples out of the oven when all tacky spots have just finished drying. Dried spots will be more opaque, while wet spots will be shiny. This may require frequent checkups.
- Samples are flexible but fragile! Take care when removing them from the mold.

## STEP SEVEN: Trimming the Sample



- Use a sharp X-Acto knife and a straightedge when trimming.
- We recommend using a clamp to make sure the straightedge does not wander during cutting.
  - If there are any bad spots in the final film, consider trimming it off.
  - Keep in mind however, that the sample needs to be big enough to fit in the tensile testing jaws.
- If there is a time gap between trimming and tensile testing, store the film in a ziplock bag.
  - Try to remove most of the air in the bag before sealing.
  - Place something flat and heavy (like a book) over the sample to make sure the film remains flat during storage.
- If there are any questions about this procedure, ask Dr. Harding for contact information.